

Electron-beam-generated plasmas for materials processing

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Abstract

The results of investigations aimed at characterizing pulsed, electron-beam-produced plasmas for use in materials processing applications are discussed. In situ diagnostics of the bulk plasma and at the plasma/surface interface are reported for plasmas produced in Ar, N₂, and mixtures thereof. Langmuir probes were employed to determine the local electron temperature, plasma density, and plasma potential within the plasma, while ion energy analysis and mass spectrometry were used to interrogate the ion flux at an electrode located adjacent to the plasma. The results illustrate the unique capabilities of electron-beam-produced plasmas and the various parameters available to optimize operating conditions for applications such as nitriding, etching, and thin film deposition.

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1. Introduction

The Naval Research Laboratory is developing a plasma-based materials modification system using a plasma source driven by a high-energy electron beam (2.0 keV). A magnetically confined sheet of electrons is used to ionize a background gas, thus producing a high-density plasma ($n_p > 10^{11} \text{ cm}^{-3}$) over the volume of the beam [1,2]. The system is currently being utilized in a number of applications including etching [3] nitriding [4], thin film deposition, and polymer surface activation.

Several features separate electron-beam-produced plasmas from conventional plasma sources, most of which are derived from the fact that the ionization process is driven by an energetic electron beam.

1.1. Low electron temperature

For plasmas produced in molecular gases, typical electron temperatures are found to be less than 1.0 eV [5]. The temperature is low because electrons created by gas ionization are cooled by elastic and inelastic collisions but are not heated by external fields, because they are not required to sustain the discharge. The electron temperature determines

the plasma potential [6] and, thus, ions incident to grounded surfaces will exhibit low energies [7].

1.2. Ion production

In addition to being an exceptionally efficient method of plasma production [1], electron beam ionization has the potential to generate a wide range of ion species, depending on the gas or gas mixture. For mixtures, the production of ions for a given gas component is approximately proportional to the concentration of that component.

1.3. Localized plasma source

The plasma production region is limited to the beam volume, which is well defined when the beam is magnetically collimated. Outside the beam channel, the electron temperature, plasma density, and ion composition are altered by ion–electron, ion–neutral, and ion–ion reactions. Because the electron beam is not tied to the chamber geometry, electrodes (or substrates) can be independently positioned to take advantage of the changes in the outwardly diffusing ions and radicals.

1.4. Scalability

The dimensions of the plasma source are tied to the electron beam dimensions. The beam thickness and width

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are determined by the electron beam source and the length is determined by the beam energy and operating pressure.

These attributes allow for a unique ability to regulate fundamental plasma parameters such as the plasma density, electron temperature, and ion composition uniformly over large areas. This is particularly important in processing applications, because these parameters will determine the flux of ions and radicals as well as the incident ion energies at the workpiece. It is critical, therefore, to characterize both the bulk plasma and the flux of species at the surface, and to determine the relationship between the two.

In this paper, experiments designed to quantify the characteristics of pulsed, electron-beam-generated plasmas produced in Ar, N₂ and their mixtures are discussed. Langmuir probe measurements of the bulk plasma density (n_p), electron temperature (T_e), and plasma potential (V_p) are presented. The results are correlated with mass-resolved ion energy distributions and flux measurements at electrode surfaces located adjacent to the plasmas. The measurements are time-resolved and taken at a grounded and biased electrode over a range of operating pressures and gas

compositions. The results illustrate the important features and advantages of electron-beam-generated plasmas and highlight the various control variables available to optimize processing parameters.

2. Experimental

A number of different systems are currently in use for materials processing and diagnostics. While the chamber geometries vary, all systems operate in a similar fashion and consist of a magnetically collimated, sheet electron beam produced by a hollow cathode. In materials processing systems, the diagnostics are absent and the materials to be processed are mounted on a stage with adjustable position, bias, and temperature control capabilities.

2.1. Chamber

The experimental apparatus used here is schematically represented in Fig. 1 and has been previously discussed

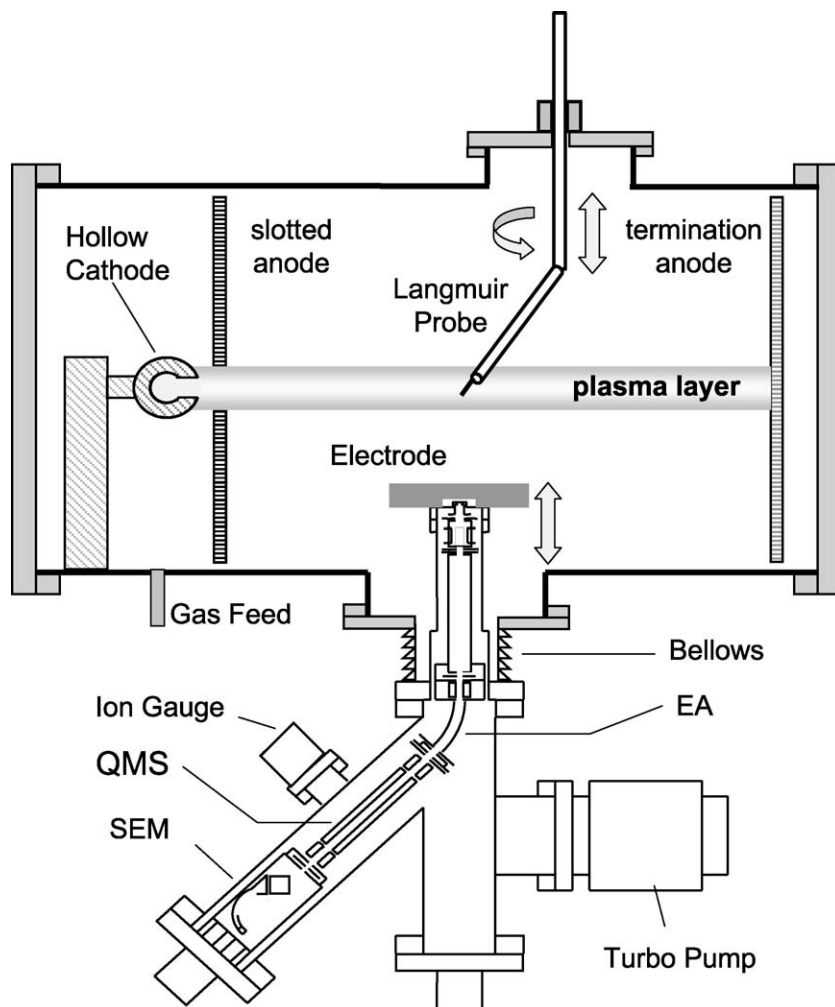


Fig. 1. Schematic diagram of the experimental apparatus.

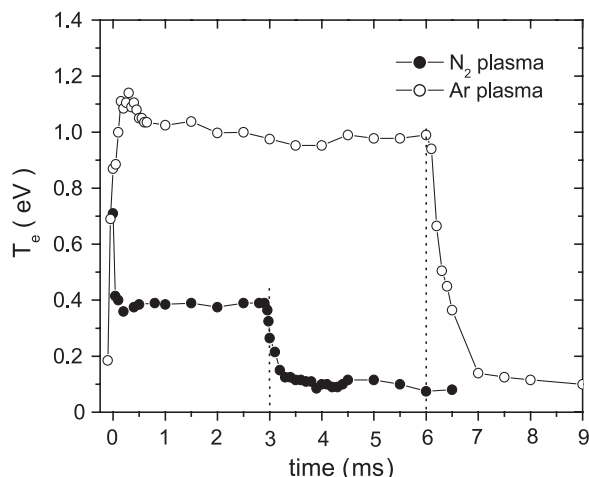


Fig. 2. The electron temperature measured along the electron beam axis in pulsed, electron-beam-generated plasmas produced in 6.7 Pa of Ar and N_2 , respectively.

[7,8]. The chamber is approximately 70-cm long, 25-cm tall, and 100-cm wide (into the page). The vacuum is maintained by a 2000 l/s turbomolecular pump and the chamber base pressure is $\sim 1 \times 10^{-5}$ Pa. High-purity gases (99.999%) are introduced via mass flow controllers. Operating pressures are achieved by selecting a flow rate and varying the conductance through a manual gate valve at the entrance to the pump. External to the chamber are magnetic field coils that produce a 150 Gauss field along the center of the chamber. The field strength varies by less than 10% over the region of interest.

2.2. Plasma production

The plasma was produced by an electron beam extracted from a linear hollow cathode. A detailed description of the hollow cathode and electron beam production can be found in Ref. [3]. The cathode was driven by a negative voltage pulse (-2 kV) and generates a sheet-like electron beam commensurate with the applied voltage. The emergent beam passed through a slot in a grounded anode before termination at a second anode. The beam volume between the anodes defines the plasma source region, where the dimensions were set by the slot size (1×25 cm) and the anode separation (43 cm). The magnetic field eliminates beam spreading via collisions with the background gas, so beam thickness is retained within an electron gyroradius ($r_{ce} \leq 1.0$ cm). The beam pulse width and duty cycle were varied between 1 and 6 ms and 10% to 50%, respectively.

2.3. Plasma diagnostics

The plasma density, T_e , and V_p were determined through the use of a Langmuir probe, as described in Ref. [5]. The body of the probe was constructed from alumina and

stainless steel and contained a nichrome wire heater to keep the probe surface clean. The probe was a 128- μ m-diameter tungsten wire and extended 2 mm from the ceramic housing. The probe was mounted on a differentially pumped, multimotion feedthrough. Linear motion set the position perpendicular to the beam, and rotary motion allowed for positioning along an arc in a plane parallel to the beam.

Ion fluxes and energy distributions were measured at a 5.7-cm-diameter stainless steel electrode using a Hiden EQP 300 Plasma Probe (Fig. 1). The probe is differentially pumped and consists of an electrostatic ion-energy analyzer (EA) in series with a quadrupole mass spectrometer (QMS). Ions enter the EQP through a small-diameter aperture (20–50 μ m) located in the center of the electrode and are collimated and focused onto the entrance of the energy analyzer by a series of electrostatic lenses. The ions are then energy selected and mass filtered before detection by a channeltron secondary-electron multiplier (SEM). Time resolution was achieved using both a fixed and scanning gate on the EQP output such that the signal was only accumulated during a given time interval [9]. For both methods, the signal was accumulated over several hundred pulses to achieve a reasonable signal-to-noise ratio.

3. Results and discussion

3.1. Production in Ar and N_2

Plasmas were produced in both atomic and molecular gases to help develop a better understanding of plasma production and decay. To this end, plasmas were produced

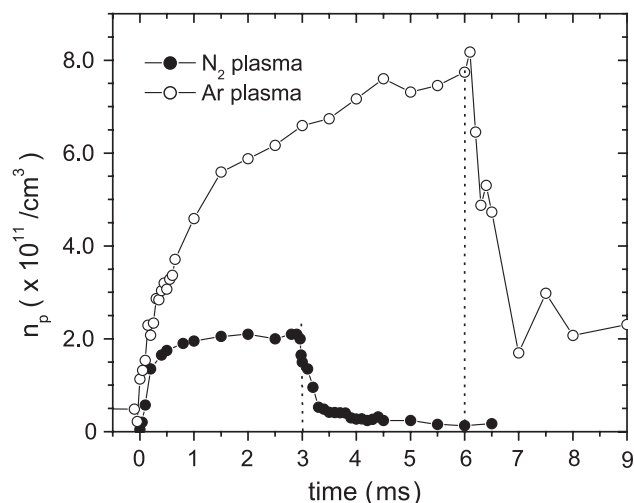


Fig. 3. The plasma density measured along the electron beam axis in pulsed, electron-beam-generated plasmas produced in 6.7 Pa of Ar and N_2 , respectively.

in 6.7 Pa of Ar and N₂, separately, and the results are shown in Figs. 2–4. For reasons that will be apparent, the pulse width was set to 6 ms in Ar and 3 ms in N₂. For both gases, the duty cycle was 10% to ensure the plasma completely decayed between pulses. The Langmuir probe was positioned on the beam axis and central to the EQP sampling electrode, which was located 2.5 cm from the beam axis.

The results of the Langmuir probe measurements are shown in Figs. 2 and 3. Both plasmas exhibit similar temporal behavior. Specifically, T_e initially spikes, then reaches steady state, and finally decays in the afterglow. The density rises smoothly to a steady state value before decaying in the afterglow. While the general trends in these two gases are similar, significant differences are apparent. First, the Ar plasmas have a higher T_e and density, and, second, they evolve slower. That is, more time is required to reach a steady state and also to decay.

It is important to recognize that gas phase reactions play a significant role in the evolution of electron-beam-generated plasmas. In the absence of externally applied electric fields, inelastic electron-neutral collisions rapidly cool the plasma electrons in molecular gases like N₂. In Ar, the

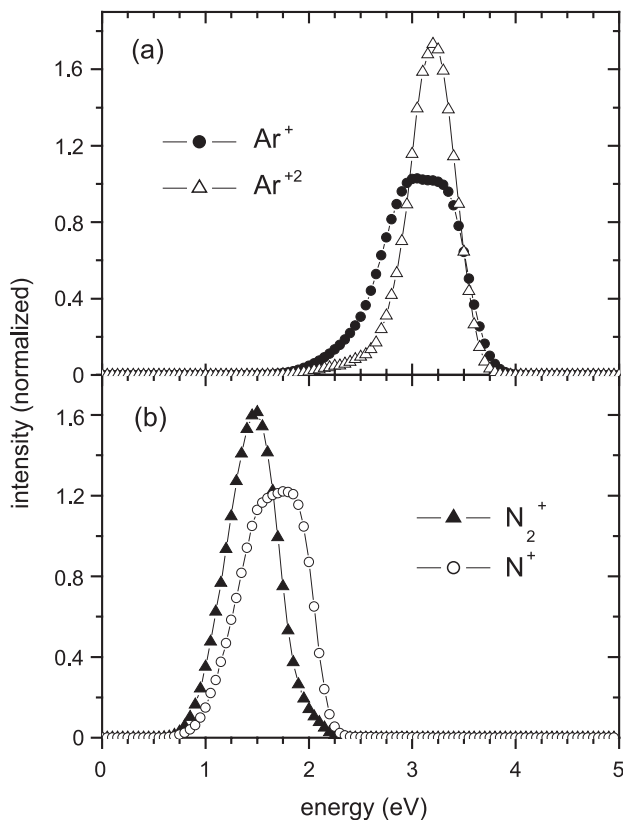


Fig. 4. Ion energy distributions measured at an electrode located 2.5 cm from the electron beam axis in plasmas produced in (a) Ar and (b) N₂. The distributions were accumulated during the electron beam pulse and normalized to the total flux of each species, respectively.

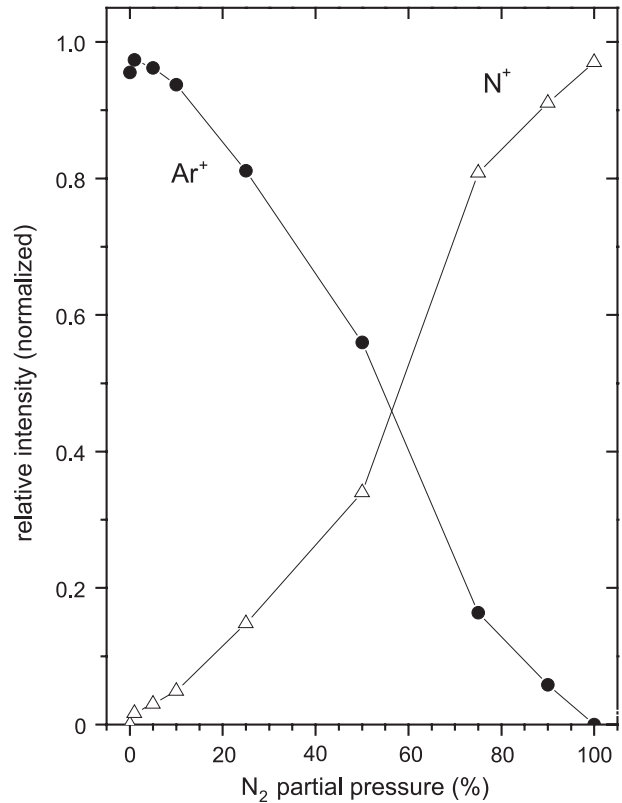


Fig. 5. The normalized flux of ions as a function of N₂ concentration. The total pressure was held constant (11.3 Pa) and the partial pressure of Ar and N₂ were adjusted accordingly. The flux of each species is normalized to the total flux.

lowest excitation level is ≈ 11 eV while in N₂, vibrational and rotational levels extend down to a few tenths of an eV. Thus, T_e is expected to be lower in N₂ (or any molecular

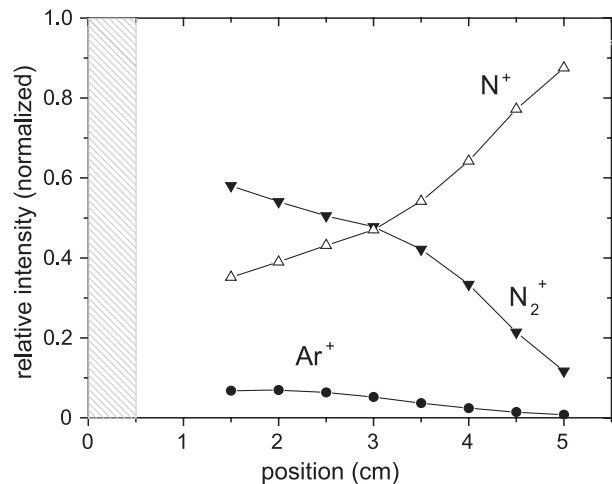


Fig. 6. The normalized flux of ions as a function of electrode location for a plasma produced in a mixture of N₂ and Ar. The flux of each species is normalized to the total flux and the shaded area represents the approximate beam half-width.

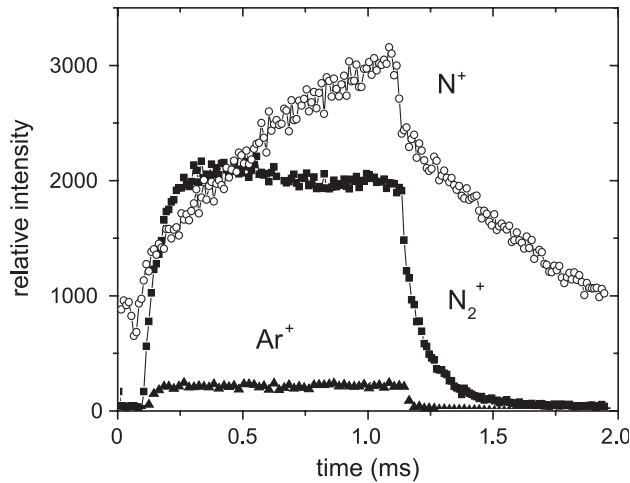


Fig. 7. The temporally resolved ion fluxes at an electrode located 3.5 cm from the electron beam axis for plasmas produced in N_2/Ar mixtures.

gas). A low T_e also enhances electron–ion recombination for molecular ions. The reaction



has an appreciable rate ($k_r \sim 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) [10] while the two-body reaction for atomic ions like Ar^+ ,



is negligible ($k_r \sim 10^{-13} \text{ cm}^3 \text{ s}^{-1}$) [11]. The dominant loss mechanism for Ar^+ ions in an argon plasma is diffusion to the walls, a comparatively slower process. Because the loss rate is smaller for Ar plasmas, the density is generally higher but evolves slower.

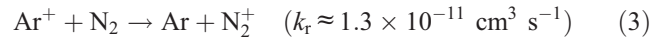
Differences between the two plasmas are also evident in the ion energy distributions of Fig. 4. The distributions were accumulated over the steady state period and normalized accordingly. The distributions in N_2 plasmas exhibit a lower average energy than the Ar distributions and these differences follow from the differences in T_e . Recall that the incident ion energy is determined by the sheath voltage at a given surface and by the probability that ions traverse the sheath without colliding. The sheath voltage is set by T_e , and thus elevated ion energies in the Ar plasma are expected.

The large electron–ion recombination loss rate in N_2 plasmas leads to a significantly larger N^+ ion density than

in conventional plasma sources. This reaction is particularly important outside the plasma production volume and leads to a reduction in the N_2^+ ion flux at remotely located surfaces. From the raw (not normalized) data of Fig. 4, the N_2^+/N^+ ion flux ratio is ≈ 1.0 , considerably smaller than expected production ratio of ≈ 4.0 [12]. By comparison, the Ar^{+2}/Ar^+ ion ratio ≈ 0.03 and comparable to the production ratio [13].

3.2. Production in N_2/Ar mixtures

Processing applications utilizing this electron-beam-based system under study in our laboratory include nitriding [4,14] and thin film deposition, both of which use plasmas produced in mixtures of N_2 and Ar. One of the unique features of electron-beam-generated plasmas is that the production of ions and radicals is largely determined by the gas concentrations and the relative ionization cross sections, which are almost independent of electron energy (above 1 keV). However, electron–ion (recombination) and ion–neutral (charge exchange) reactions will affect the fluxes. This is illustrated in Fig. 5, where the normalized flux of ions at the EQP electrode as a function of N_2 concentration is shown. In addition to reaction (1) above, the reaction [15]



is thought to play an important role in determining the fluxes. The dominant loss mechanism for N^+ is assumed to be diffusion.

Results from experiments designed to emulate conditions of a plasma-based nitriding of stainless steel [4] are shown in Figs. 6 and 7. The operating pressure was approximately 21.3 Pa (12% Ar by pressure), the pulse width was 1 ms, and the duty factor was 50%. For the results of Fig. 6, the fluxes were accumulated over the entire period at increasing EQP electrode distances and show a strong spatial dependency. For distances greater than 3 cm, N^+ dominates. Shown in Fig. 7 is the flux temporal profile with the EQP electrode located at 3.5 cm. It is evident that the dominance of N^+ results from its persistence over all time, particularly in the afterglow where N_2^+ and Ar^+ rapidly decay. Here again we can attribute the large N^+ flux to the gas phase reactions mentioned above.

Table 1

The results of Langmuir probe measurements at arbitrary locations along the electron beam axis

Location (arbitrary)	Grounded anode			25-V anode bias			50-V anode bias		
	V_p (V)	T_e (eV)	$n_p \times 10^{11} \text{ (cm}^{-3}\text{)}$	V_p (V)	T_e (eV)	$n_p \times 10^{11} \text{ (cm}^{-3}\text{)}$	V_p (V)	T_e (eV)	$n_p \times 10^{11} \text{ (cm}^{-3}\text{)}$
1	1.9	0.5	1.8	25.9	0.4	2.0	50.7	0.4	1.9
2	2.2	0.6	2.4	25.9	0.6	2.2	51.0	0.6	2.2
3	2.2	0.6	2.1	25.7	0.6	1.8	50.6	0.5	1.6
4	1.9	0.5	2.0	25.7	0.6	2.0	50.5	0.5	1.4

The plasma potential (V_p), electron temperature (T_e), and plasma density (n_p) are listed for grounded and biased termination anodes.

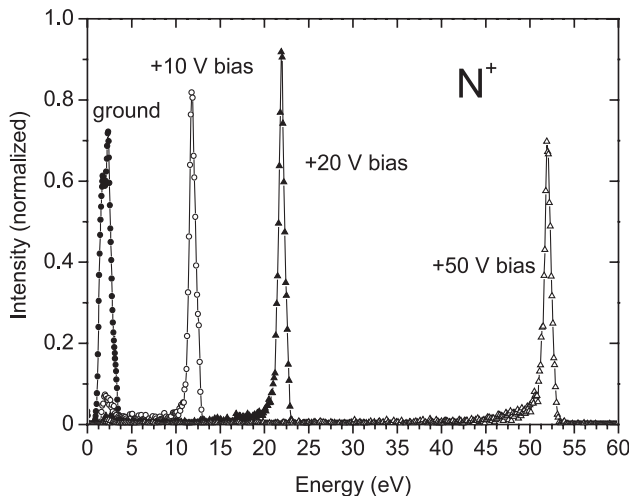


Fig. 8. N^+ energy distributions at an electrode located adjacent to plasmas produced in N_2 . The electrode was grounded and various biases were applied to the termination anode.

This unique variation in the ion flux composition, particularly with distance, is found to influence the nitriding rate of stainless steel [14].

3.3. Biasing techniques

Processing applications often require an elevated ion energy, and to this end a bias is commonly applied to the workpiece. An alternative method of increasing the ion energies is to elevate the plasma potential, and this can be achieved by positively biasing a surface in contact with the plasma [16]. For large substrates, this method is only useful if the plasma potential is uniformly elevated such that the incident ion energies are uniform over the entire substrate. To test this concept, the termination anode was biased and the results are shown in Table 1 and Fig. 8.

Table 1 summarizes the results of Langmuir probe measurements at various locations along the electron beam axis for plasmas produced in N_2 (8 Pa). The probe was rotated through an arc, yielding measurements at arbitrary positions along the beam axis. As a reference, position 3 was central to the EQP electrode, while positions 1 and 4 were within 2 cm of either anode. All reported data are 2.5 ms into a 3.0-ms pulse. The results show a uniform plasma potential that lies ≈ 1 V above the applied biases of 25 and 50 V. For comparison, the plasma potential (≈ 2 V) for a grounded anode is also shown. The plasma density and T_e are also found to be reasonably uniform and independent of the applied bias.

The N^+ energy distributions at the grounded EQP electrode for various anode biases are shown in Fig. 8. A majority of the incoming ions impact the electrode with energies slightly above the bias value (and thus comparable to the plasma potential), suggesting that N^+ ions suffer few collisions while crossing the sheath. As noted, the low T_e

leads to a low plasma potential, which in turn reduces the breadth of the energy distributions. The results indicate that the width remains small when the bias is elevated and thus the ion energy can be tuned to a narrowly defined value, which can be particularly useful when a specific energy is required.

4. Summary

Experiments were performed to characterize pulsed, electron-beam-generated plasmas in Ar, N_2 , and their mixtures. The results illustrate some of the useful attributes of these plasmas. The plasmas were found to have densities above 10^{11} cm^{-3} and electron temperatures below 1.5 eV. This allows for large fluxes of low-energy ions in the absence of applied bias. If higher energies are required, biasing of the substrate or termination anode can be employed. Because of the low electron temperatures, ion energies were nearly equal to the applied bias.

The plasma production region is limited to the electron beam volume, and within that volume, ion production is largely governed the beam energy, current, total pressure, and the partial pressures of the gases in the mixture. For positions outside the beam, ion–neutral and ion–electron reactions strongly influence the electron temperature, density, and ion composition.

These features provide a unique ability to regulate plasma production and control the ion fluxes and energies at electrodes located adjacent to the plasma. The control variables include the electron beam pulse width, the duty cycle, the gas pressure or partial pressure, the applied bias, and the electrode location. This unique ability provides pulsed, electron-beam-produced plasmas with a broad range of process control that can be useful in a variety of processing applications.

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References

- [1] R.F. Fernsler, W.M. Manheimer, R.A. Meger, J. Mathew, D.P. Murphy, R.E. Pechacek, J.A. Gregor, *Phys. Plasmas* 5 (1998) 2137.
- [2] W.M. Manheimer, R.F. Fernsler, M. Lampe, R.A. Meger, *Plasma Sources Sci. Technol.* 9 (2000) 370.
- [3] D. Leonhardt, C. Muratore, S.G. Walton, D.D. Blackwell, R.F. Fernsler, R.A. Meger, *Surf. Coat. Technol.* 177–178 (2004) 682.
- [4] C. Muratore, D. Leonhardt, S.G. Walton, D.D. Blackwell, R.F. Fernsler, R.A. Meger, *Surf. Coat. Technol.* (2004) (submitted for publication).
- [5] D. Leonhardt, S.G. Walton, D.D. Blackwell, W.E. Amatucci, D.P. Murphy, R.F. Fernsler, R.A. Meger, *J. Vac. Sci. Technol., A* 19 (2001) 1367.

- [6] M.A. Lieberman, M.J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley, New York, 1994.
- [7] S.G. Walton, D. Leonhardt, D.D. Blackwell, R.F. Fernsler, D.P. Murphy, R.A. Meger, *J. Vac. Sci. Technol., A* 19 (2001) 1325.
- [8] S.G. Walton, D. Leonhardt, R.F. Fernsler, R.A. Meger, *Appl. Phys. Lett.* 83 (2003) 626; *Appl. Phys. Lett.* 81 (2002) 987.
- [9] S.G. Walton, D. Leonhardt, D.D. Blackwell, R.F. Fernsler, D.P. Murphy, R.A. Meger, *Phys. Rev., E* 65 (2002) 046412.
- [10] F.J. Mehr, M.A. Biondi, *Phys. Rev.* 181 (1969) 264.
- [11] D.R. Bates, A. Dalgarno, in: D.R. Bates (Ed.), *Atomic and Molecular Processes*, Academic Press, New York, 1962.
- [12] H.C. Straub, P. Renault, B.G. Lindsay, K.A. Smith, R.F. Stebbings, *Phys. Rev., A* 54 (1996) 2146.
- [13] H.C. Straub, P. Renault, B.G. Lindsay, K.A. Smith, R.F. Stebbings, *Phys. Rev., A* 52 (1995) 1115.
- [14] C. Muratore, S.G. Walton, D. Leonhardt, R.F. Fernsler, D.D. Blackwell, R.A. Meger, *J. Vac. Sci. Technol., A* (2004) (submitted for publication).
- [15] W. Lindinger, F. Howorka, P. Lukas, S. Kuhn, H. Villinger, E. Alge, H. Ramler, *Phys. Rev., A* 23 (1980) 2319.
- [16] J.W. Coburn, E. Kay, *J. Appl. Phys.* 43 (1972) 4695.